Particle in a box states

For free particles we will often consider the quantum single particle states to be "particle in a box" states.

We take our system to have length $L$ in each direction $x$, $y$, $z$, volume $V = L^3$. We also use periodic boundary conditions

\[ \phi(x + L, y, z) = \phi(x, y, z), \quad \phi(x, y + L, z) = \phi(x, y, z), \]
\[ \phi(x, y, z + L) = \phi(x, y, z) \]

Energy eigenstates can then be taken as

\[ \phi_k(r) = \frac{1}{\sqrt{V}} e^{i \vec{k} \cdot \vec{r}} \]
with energy \( E_k = \frac{\hbar^2 k^2}{2m} \)

\[ \hbar = \frac{L}{2\pi} \] with $\hbar$ Planck's constant.

Periodic boundary conditions require

\[ \Rightarrow \phi_k(x + L, y, z) = \frac{1}{\sqrt{V}} e^{i \vec{k} \cdot (x + L)} e^{i k y} e^{i k z} \]
\[ \Rightarrow \phi_k(x, y, z + L) = \frac{1}{\sqrt{V}} e^{i k x} e^{i k y} e^{i k z} \]
\[ \Rightarrow e^{i k x L} = 1 \Rightarrow \ k_x = \frac{2\pi}{L} n_x \text{ with } n_x = 0, \pm 1, \pm 2, \ldots \text{ integer} \]

Similarly \( k_y = \frac{2\pi}{L} n_y \) and \( k_z = \frac{2\pi}{L} n_z \).

Spacing between allowed values of $k_x$ (or $k_y$ or $k_z$) is \( \frac{2\pi}{L} \).
Consider a non-interacting two particle system

Compute $\langle \vec{r}_1, \vec{r}_2 \mid e^{\beta \hat{H}} \mid \vec{r}_1, \vec{r}_2 \rangle$ diagonal elements of $\hat{H}$ in position basis by probability one particle is at $\vec{r}_1$ and the other is at $\vec{r}_2$

For free non-interacting particles, the energy eigenstates are specified by two wave vectors $\vec{k}_1, \vec{k}_2$ with $E = \frac{k_1^2 + k_2^2}{2m}$.

The eigenstates are symmetrized plane waves $\phi_k(r) = \frac{1}{\sqrt{V}} e^{i \vec{k} \cdot \vec{r}}$.

The eigenstates are symmetrized plane waves

$$\langle \vec{r}_1, \vec{r}_2 \mid e^{\beta \hat{H}} \mid \vec{r}_1, \vec{r}_2 \rangle = \sum_{\vec{k}_1, \vec{k}_2} \frac{e^{-\beta \frac{\hbar^2}{2m} \left( k_1^2 + k_2^2 \right)}}{Q_2} \langle \vec{k}_1, \vec{k}_2 \mid e^{\beta \hat{H}} \mid \vec{k}_1, \vec{k}_2 \rangle$$

$$= \frac{1}{Q_2} \sum_{\vec{k}_1, \vec{k}_2} e^{-\beta \frac{\hbar^2}{2m} \left( k_1^2 + k_2^2 \right)} |\langle \vec{k}_1, \vec{k}_2 \mid e^{\beta \hat{H}} \mid \vec{k}_1, \vec{k}_2 \rangle|^2$$

Note, if we take $\vec{k}_1 \rightarrow \vec{k}_2$ and $\vec{k}_2 \rightarrow \vec{k}_1$, then $\langle \vec{r}_1, \vec{r}_2 \mid \vec{k}_1, \vec{k}_2 \rangle = \pm \langle \vec{r}_1, \vec{r}_2 \mid \vec{k}_2, \vec{k}_1 \rangle$

Since the matrix element is symmetric in the above sum, any sign change is canceled out. Thus in taking the sum over all eigenstates, we can replace $\sum$ by independent sums on $\vec{k}_1$ and $\vec{k}_2$ provided we multiply by $\frac{1}{2!}$, so as not to double count $\langle \vec{k}_1, \vec{k}_2 \rangle$ and $\langle \vec{k}_2, \vec{k}_1 \rangle$ which represent the same physical state.

$$\langle \vec{r}_1, \vec{r}_2 \mid e^{\beta \hat{H}} \mid \vec{r}_1, \vec{r}_2 \rangle = \frac{1}{2!} \sum_{\vec{k}_1, \vec{k}_2} e^{-\beta \frac{\hbar^2}{2m} \left( k_1^2 + k_2^2 \right)} |\langle \vec{k}_1, \vec{k}_2 \mid e^{\beta \hat{H}} \mid \vec{k}_1, \vec{k}_2 \rangle|^2$$
So
\[ \int_{\gamma} e^{-2k^2 + i2k'} \, dz = \left( \frac{2\pi k}{2} \right)^2 e^{-\frac{1}{2}k^2} \]
where \( k = \frac{k}{1+i} \).

Next, let \( x = \frac{1}{2} \).

We need the following integral:
\[ \int_{\gamma} e^{-2k^2 + i2k} \, dz = \frac{e^{-\frac{1}{2}k^2}}{(2\pi k)^2} \]
where \( k = \frac{k}{1+i} \).

Then, let \( x = \frac{1}{2} \).

\[ \int_{\gamma} e^{-2k^2 + i2k} \, dz = \frac{e^{-\frac{1}{2}k^2}}{(2\pi k)^2} \]
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Finally, let \( x = \frac{1}{2} \).

\[ \int_{\gamma} e^{-2k^2 + i2k} \, dz = \frac{e^{-\frac{1}{2}k^2}}{(2\pi k)^2} \]
where \( k = \frac{k}{1+i} \).
So 
\[ \langle \vec{r}_1 \vec{r}_2 \rangle e^{-\beta \hat{H}} | \vec{r}_1 \vec{r}_2 \rangle = \frac{1}{2(2\pi)^6} \left( \frac{2\pi}{\alpha} \right)^3 \left[ 1 \pm e^{-\frac{r_{12}^2}{\alpha^2}} \right] \]

\[ = \frac{1}{2(2\pi\lambda^6)^3} \left[ 1 \pm e^{-\frac{\vec{r}_{12}^2}{\lambda^2}} \right] \]

It is customary to introduce the thermal wavelength $\lambda$ by
\[ \lambda^2 = 2\pi \alpha = \frac{2\pi \hbar^2}{m} = \frac{2\pi \hbar^2}{k_B T} = \frac{h^2}{2\pi m k_B T} \]

Then
\[ \langle \vec{r}_1 \vec{r}_2 \rangle e^{-\beta \hat{H}} | \vec{r}_1 \vec{r}_2 \rangle = \frac{1}{2\lambda^6} \left[ 1 \pm e^{-\frac{2\pi \vec{r}_{12}^2}{\lambda^2}} \right] \]

Now we need
\[ Q_2 = \int d^3r_1 \int d^3r_2 \langle \vec{r}_1 \vec{r}_2 \rangle e^{-\beta \hat{H}} | \vec{r}_1 \vec{r}_2 \rangle \]

\[ = \frac{1}{2\lambda^6} \int d^3r_1 \int d^3r_2 \left[ 1 \pm e^{-\frac{2\pi \vec{r}_{12}^2}{\lambda^2}} \right] \]

Let \[ \vec{r} = \frac{\vec{r}_1 + \vec{r}_2}{2} \]
\[ \vec{r}' = \vec{r}_1 - \vec{r}_2 = \vec{r}_{12} \]

From stefan\-bolzman
\[ \frac{1}{2\lambda^6} \left[ 1 \pm \int_{\vec{r}}^{\infty} 4\pi r^2 e^{-\frac{2\pi r^2}{\lambda^2}} dr \right] \]

\[ = \frac{1}{2\lambda^6} \left[ 1 \pm 4\pi \int_{\vec{r}}^{\infty} \frac{r^2}{\lambda^2} e^{-\frac{4\pi r^2}{\lambda^2}} dr \right] \]

\[ \approx \frac{1}{2} \left( \frac{V}{\lambda^3} \right)^2 \] as $V \to \infty$
So \( \left\langle \vec{r}_1, \vec{r}_2 \left| \hat{\rho} \right| \vec{r}_1, \vec{r}_2 \right\rangle = \frac{1}{2\hbar^2} \left[ 1 \pm e^{-\frac{2\pi r_{12}^2}{\lambda^2}} \right] \)

\[
\left\langle \vec{r}_1, \vec{r}_2 \left| \hat{\rho} \right| \vec{r}_1, \vec{r}_2 \right\rangle = \frac{1}{\sqrt{2}} \left[ 1 \pm e^{-\frac{2\pi r_{12}^2}{\lambda^2}} \right]
\]

+ bosons

- fermions

= probability one particle is at \( \vec{r}_1 \) and the other is at \( \vec{r}_2 \)

Consider two classical non-interacting particles. Since the positions of these particles are uncorrelated, we have

\[
\left\langle \vec{r}_1, \vec{r}_2 \left| \hat{\rho} \right| \vec{r}_1, \vec{r}_2 \right\rangle = \frac{1}{\sqrt{2}}
\]

The \( \pm e^{-\frac{2\pi r_{12}^2}{\lambda^2}} \) terms are therefore introduced into the pair probability due to the quantum statistics (BE, or -FD)

For BE, using the + sign, we see

\[
\left\langle \vec{r}_1, \vec{r}_2 \left| \hat{\rho} \right| \vec{r}_1, \vec{r}_2 \right\rangle \text{ is larger than it is classically}
\]

\( \Rightarrow \) BE statistics give an effective attraction

For FD, using the - sign, we see

\[
\left\langle \vec{r}_1, \vec{r}_2 \left| \hat{\rho} \right| \vec{r}_1, \vec{r}_2 \right\rangle \text{ is smaller than it is classically}
\]

\( \Rightarrow \) FD statistics give an effective repulsion
We can treat this quantum correlation as an effective classical interaction between the two particles. For classical particles with a pair wise interaction $V(\mathbf{r}_1-\mathbf{r}_2)$, the classical prob to have one particle at $\mathbf{r}_1$ and the second at $\mathbf{r}_2$ is

$$p(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\mathbf{p}_1, \mathbf{p}_2} e^{-\beta \left( \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} + V(\mathbf{r}_2) \right)}$$

$$= \frac{\sum_{\mathbf{p}_1, \mathbf{p}_2} e^{-\beta \left( \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} + V(\mathbf{r}_2) \right)}}{\sum_{\mathbf{r}_1, \mathbf{r}_2} e^{-\beta V(\mathbf{r}_2)}}$$

sufficiently fast

For large $V$, ad assuming $V(\mathbf{r}_2) \to 0$ as $\mathbf{r}_2 \to \infty$

$$\sum_{\mathbf{r}_1, \mathbf{r}_2} e^{-\beta V(\mathbf{r}_2)} = \sum_{\mathbf{r}_1} \sum_{\mathbf{r}_2} e^{-\beta V(\mathbf{r}_2)} = \sqrt{V} \sum_{\mathbf{r}_2} e^{-\beta V(\mathbf{r}_2)}$$

center of mass coord $\mathbf{r} \sim \sqrt{V}$

$$p(\mathbf{r}_1, \mathbf{r}_2) = \frac{e^{-\beta V(\mathbf{r}_2)}}{\sqrt{V}}$$

Compare with our expressions from quantum statistics.

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \hat{p} | \mathbf{r}_1, \mathbf{r}_2 \rangle = \frac{1}{\sqrt{V}} \left[ 1 \pm e^{-\frac{2\pi \mathbf{r}_1 \cdot \mathbf{r}_2}{\lambda^2}} \right]$$
\[ U(r) = -k_B T \ln \left[ 1 \pm e^{-\frac{2\pi r^2}{\lambda^2}} \right] \]

For BE, \(-\) for FD

\[ \lambda^2 = \frac{2\pi \beta \hbar^2}{m} = \frac{2\pi^2 \hbar^2}{m k_B T} = \frac{\hbar^2}{2\pi^2 m k_B T} \]

we can plot these as

![Graph showing BE and FD potentials](attachment:fig5_1.png)

we see that the BE statistics lead to an effective attraction while FD statistics lead to an effective repulsion, for small separations

\[ \gamma < \lambda \]

thermal wavelength \( \lambda = \sqrt{\frac{\hbar^2}{2\pi^2 m k_B T}} \)

sets the length scale below which quantum effects are important for the correlation between the positions of two particles.
$N$-particles

eigenstates $\langle \vec{r}_1 \cdots \vec{r}_N | \vec{k}_1 \cdots \vec{k}_N \rangle = \frac{1}{N! \cdot V^N} \sum_{\mathbf{p}} (\pm)^{\mathbf{p}} e^{i \sum_{\mathbf{p}} (\mathbf{p} \cdot \vec{k}_i)^* \cdot \vec{k}_i}$

where $\mathbf{p} \cdot \vec{k}_i$ is the permutation of position $\vec{r}_i$

we get $\mathbf{p}(123) = 23$ then $P1 = 2$, $P2 = 3$ and $P3 = 1$

$\langle \vec{r}_1 \cdots \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1 \cdots \vec{r}_N \rangle = \sum_{\vec{k}_1 \cdots \vec{k}_N} e^{-\frac{\beta}{2} \sum_{i} (k_i^2 + \cdots + k_N^2)} \langle \vec{r}_1 \cdots \vec{r}_N | \vec{k}_1 \cdots \vec{k}_N \rangle^2$

$|\langle \vec{r}_1 \cdots \vec{r}_N | \vec{k}_1 \cdots \vec{k}_N \rangle|^2 = \frac{1}{N! \cdot V^N} \sum_{\mathbf{p}} \sum_{\mathbf{p'}} (\pm)^{\mathbf{p} \cdot \mathbf{p'}} e^{i \sum_{\mathbf{p}} [\mathbf{p} \cdot \vec{k}_i - \mathbf{p'} \cdot \vec{k}_i]^* \cdot \vec{k}_i}$

Note: we can write $[\mathbf{p} \cdot \vec{k}_i - \mathbf{p'} \cdot \vec{k}_i]^* \cdot \vec{k}_i = [\mathbf{p} - \mathbf{p'} \cdot \vec{k}_i]^* \cdot \vec{k}_i$

where $\mathbf{p'}$ is inverse permutation of $\mathbf{p}$

and $(\pm)^{\mathbf{p'}} = (\pm)^{\mathbf{p}^*}$

$|\langle \vec{r}_1 \cdots \vec{r}_N | \vec{k}_1 \cdots \vec{k}_N \rangle|^2 = \frac{1}{N! \cdot V^N} \sum_{\mathbf{p}} \sum_{\mathbf{p''}} (\pm)^{\mathbf{p} \cdot \mathbf{p''}} e^{i \sum_{\mathbf{p}} (\vec{r}_i - \mathbf{p''} \cdot \vec{k}_i)^* \cdot \mathbf{p} \cdot \vec{k}_i}$

where $\mathbf{p}' = \mathbf{p} \cdot \mathbf{p''}$

Now, when we sum over the energy eigenstates, we sum over $\vec{k}_i$.

Since $\vec{k}_i$ is a dummy index in the sum, it does not matter whether we label it $\vec{k}_i$ or $\mathbf{p} \cdot \vec{k}_i$. So in the above, each term in the $\sum_{\mathbf{p}}$ contributes an equal amount.

We can therefore replace $\sum_{\mathbf{p}}$ by $N!$ times the one term with $\mathbf{p} = \mathbf{1}$ the identity. Similarly, when we do the sum on eigenstates $\sum_{\mathbf{p}} \psi$ we can do independent sums on $\vec{k}_1 \cdots \vec{k}_N$ provided $|\psi | \vec{k}_1 \cdots \vec{k}_N \rangle$ we add a factor $1/N!$ to prevent double counting.
The result is:

\[ \langle \tilde{r}_1 \cdots \tilde{r}_N | e^{-\beta H} \tilde{r}_1 \cdots \tilde{r}_N \rangle = \]

\[ \frac{1}{N! \lambda^{3N}} \sum_{\tilde{k}_1 \cdots \tilde{k}_N} e^{-\frac{\beta \hbar^2}{2m} (\tilde{k}_1^2 + \cdots + \tilde{k}_N^2)} \sum_{\mathcal{P}} \prod_{i=1}^{N} e^{i \sum_{l \in \mathcal{P}} \tilde{k}_l \cdot (\tilde{r}_l - \mathcal{P} \tilde{r}_l)} \]

\[ = \frac{1}{N! (2\pi)^{3N}} \sum_{\mathcal{P}} \prod_{i=1}^{N} \left[ \int d^3 k_i \ e^{-\frac{\beta \hbar^2}{2m} k_i^2 + i \sum_{l \in \mathcal{P}} \tilde{k}_l \cdot (\tilde{r}_l - \mathcal{P} \tilde{r}_l)} \right] \]

The integral we did when considering the two body problem.

\[ = \frac{1}{N! (2\pi)^{3N}} \sum_{\mathcal{P}} \prod_{i=1}^{N} \left[ \frac{1}{\alpha} \right] \left[ \left( \frac{2\pi}{\alpha} \right)^{3/2} e^{-\frac{(\mathcal{P} \tilde{r}_l - \mathcal{P} \tilde{r}_l)^2}{2\alpha}} \right] \]

\[ = \frac{1}{N! (2\pi)^{3N}} \sum_{\mathcal{P}} \prod_{i=1}^{N} \left[ \frac{1}{\alpha} \right] \left[ \left( \frac{2\pi}{\alpha} \right)^{3/2} e^{-\frac{(\mathcal{P} \tilde{r}_l - \mathcal{P} \tilde{r}_l)^2}{2\alpha}} \right] \]

where \( f(r) = e^{-r^2/2\alpha} \)

\[ = \frac{1}{N! \lambda^{3N}} \sum_{\mathcal{P}} \prod_{i=1}^{N} f(\tilde{r}_i - \mathcal{P} \tilde{r}_i) \]

where \( \lambda = 2\pi \alpha = 2\pi \beta \hbar^2 m \)

so \( f(0) = 1 \)

Partition function

\[ Q_N = \int d^3 r_1 \cdots d^3 r_N \langle \tilde{r}_1 \cdots \tilde{r}_N | e^{-\beta H} | \tilde{r}_1 \cdots \tilde{r}_N \rangle \]

\[ = \frac{1}{N! \lambda^{3N}} \sum_{\mathcal{P}} \prod_{i=1}^{N} \left[ \frac{1}{\alpha} \right] \left[ \left( \frac{2\pi}{\alpha} \right)^{3/2} e^{-\frac{(\mathcal{P} \tilde{r}_l - \mathcal{P} \tilde{r}_l)^2}{2\alpha}} \right] \]

\[ = \frac{1}{N! \lambda^{3N}} \sum_{\mathcal{P}} \prod_{i=1}^{N} f(\tilde{r}_i - \mathcal{P} \tilde{r}_i) \]

\[ = \frac{1}{N! \lambda^{3N}} \sum_{\mathcal{P}} \prod_{i=1}^{N} f(\tilde{r}_i - \mathcal{P} \tilde{r}_i) \cdots f(\tilde{r}_N - \mathcal{P} \tilde{r}_N) \]
Leading term is when \( P = 1 \) the identity. Then
\[
P \hat{r}_i = \bar{r}_i \quad \text{and all the } f \text{ terms are } f(0) = 1.
\]

The next order in leading terms are those corresponding to one pair exchange, say \( P \hat{r}_i = \bar{r}_j \) and \( P \bar{r}_j = \bar{r}_i \), for then only two of the \( f \) factors are not unity. The next order are terms from permutations \( P \hat{r}_i = \bar{r}_j \), \( P \bar{r}_i = \bar{r}_k \), \( P \hat{r}_k = \bar{r}_i \), three particle exchanges, etc.

\[
Q_N = \frac{\frac{V}{N}}{\frac{1}{NaN}} \left\{ 1 \pm \sum_{i<j} \frac{\int d^3r_i \int d^3r_j}{\sqrt{V}} f(\hat{r}_i - \bar{r}_j) f(\bar{r}_j - \bar{r}_i) \right. \\
+ \sum_{i<j<k} \frac{\int d^3r_i \int d^3r_j \int d^3r_k}{\sqrt{V} \sqrt{V}} f(\hat{r}_i - \bar{r}_j) f(\bar{r}_j - \bar{r}_k) f(\bar{r}_k - \bar{r}_i) \\
\left. \pm \ldots \right\}
\]

The leading term \( \frac{\frac{V}{N}}{\frac{1}{NaN}} \) is just the classical result,

provided we take the phase space parameter \( h \) to be Planck's constant. We set the Gibbs \( \frac{1}{N!} \) factor automatically.

The higher order terms are the quantum corrections arising from 2-particle, 3-particle, etc., exchanges.

For \( FD \), the terms add with alternating signs.
For \( BE \), the terms all add with (+) sign.